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Synthesis of primary-alcohol-terminated polyepichlorohydrin with molecular weight of 4000 to 12000

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Previous studies of cationic polymerization of epichlorohydrin (ECH) indicate that the commonly used initiator systems, Lewis acid/alcohol or tertiary oxonium salt/alcohol complexes give polyepichlorohydrin (PECH) whose average molecular weight is less than 4000 and the terminal groups are sterically hindered secondary alcohols. In our study, a novel pseudo-living polymerization system of epichlorohydrin has been developed, using 1,4-butaneditriflate (BDT) as the initiator. The advantages of BDT as the initiator are: (1) There are no head groups on the polymeric chains because BDT is difunctional, and (2) the tail groups (triflate esters) of the polymeric chains can be converted to a variety of functional groups. Our experimental results demonstrate that telechelic PECH having molecular weights in the range of 4000 - 15000 and with different functional groups can be synthesized. For example, the end-groups of PECH can be phenoxide groups or 1-hydroxybutyl groups; these have been characterized by UV, FTIR and NMR studies. Furthermore, PECH with different alcohol structures and the functionalities of two and four have been synthesized. Kinetic studies of these polymeric alcohols indicate that our versatile synthetic procedure can also produce PECH having

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SYNTHESIS OF PRIMARY-ALCOHOL-TERMINATED POLYEPICHLOROHYDRIN WITH MOLECULAR WEIGHT OF 4000 TO 12000

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SYNTHESIS OF PRIMARY-ALCOHOL-TERMINATED POLYEPICHLOROHYDRIN WITH MOLECULAR WEIGHT OF 4000 TO 12000

INTRODUCTION

Previous studies of cationic polymerization of epichlorohydrin (ECH) indicate that the commonly used initiator systems, Lewis acid/alcohol or tertiary oxonium salt/alcohol complexes, give polyepichlorohydrin (PECH) having average molecular weights less than 4000 and the terminal groups are primarily secondary alcohols. Although the mechanism proposed by Okamoto[1,2] and Penczek[3] has the characteristics of a pseudo-living polymerization process involving a nucleophilic attack of the alcohol groups on the protonated oxonium ion of epichlorohydrin, the average molecular weight has not exceeded 5000. Furthermore, the end-groups of the polymer are sterically hindered secondary alcohol groups and cannot be readily converted to other desired functionalities.

If telechelic PECH with varying molecular weights in the range of 4000 - 15000 and having different functional groups can be synthesized, they would have the potential for a broad range of applications. A polymerization system having this potential was discovered when 1,4-butaneditriflate (BDT) was used as the initiator.

In this report, the results of our studies have been divided into three
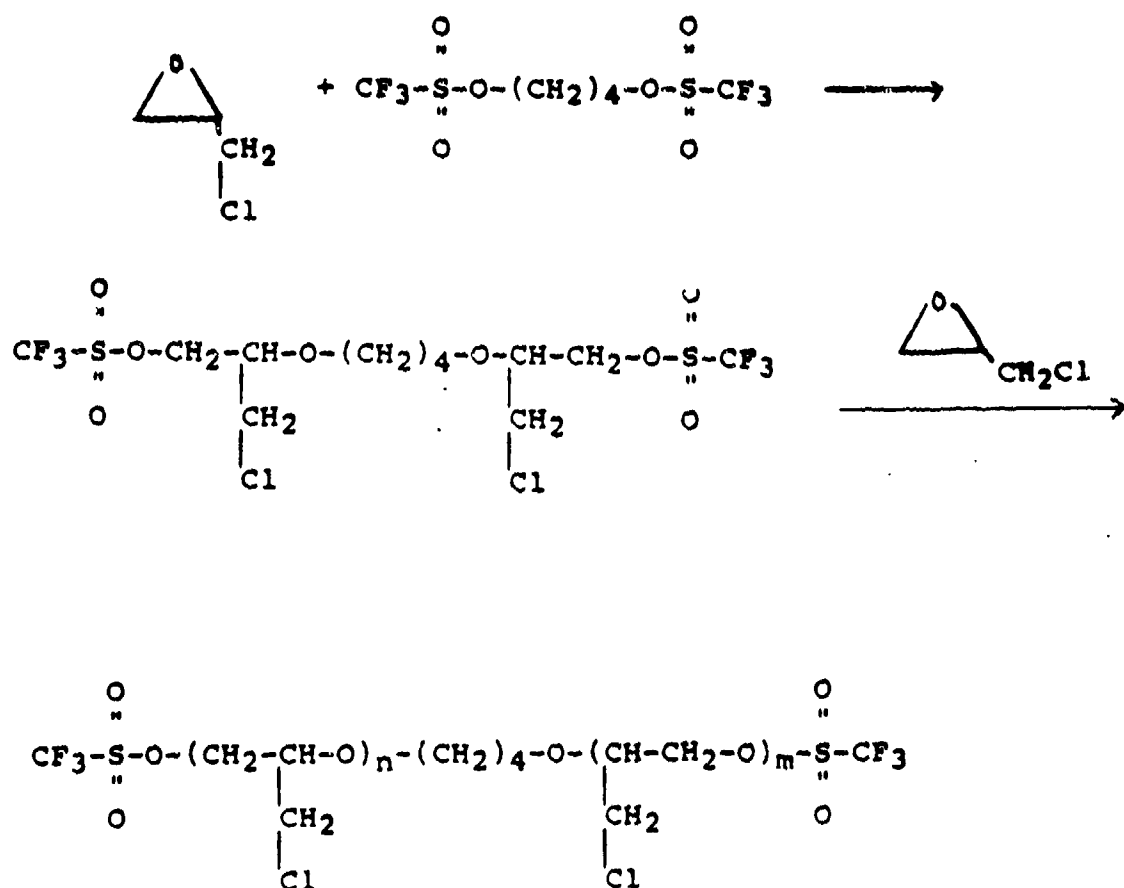
following sections and reported separately.

I.   Synthesis of Telechelic Polyepichlorohydrin (PECH)

II.   Characterization of PECH and the Kinetics of Urethane

       Formation

III.   Polyfunctional Triflates; Syntheses of Precursers.

I.   Synthesis of Telechelic Polyepichlorohydrin (PECH)

Results on polymerization of ECH using BDT and ethyltriflate (ET) are summarized in Table I.   Both initiators give the same results based on the monomer/initiator equivalent ratio, and appear to give PECH with molecular weights as high as desired. It also appears that the propagating species are still active, i.e. "living". For example, when the ECH to BDT equivalent ratio was 10, PECH with a number average molecular weight (M_n) of 6900 was obtained, after 24 hours at 25°C (item 4). Further addition of ECH and an additional 24 hours of polymerization time, resulted in PECH with M_n of 14,000 (item 6). When the second addition was made with tetrahydrofuran (THF) monomer, the resulting polymer, after 24 hours, had a M_n of 13,000. The latter is expected to be a block copolymer of ECH and THF. Number average molecular weight of these polymers were determined from GPC curves. Hence, these values are approximate and relative, although they were calibrated using standard PECH samples.

Polymerization most likely occurs through the triflate ester groups as depicted below.

$$\triangle\!\!\!\!\triangle\begin{array}{c}O\\CH_2\\|\\Cl\end{array} + CF_3-\overset{O}{\underset{O}{\overset{\|}{S}}}-O-(CH_2)_4-O-\overset{O}{\underset{O}{\overset{\|}{S}}}-CF_3 \longrightarrow$$

$$CF_3-\overset{O}{\underset{O}{\overset{\|}{S}}}-O-CH_2-\overset{CH_2}{\underset{Cl}{\overset{|}{CH}}}-O-(CH_2)_4-O-\overset{CH_2}{\underset{Cl}{\overset{|}{CH}}}-CH_2-O-\overset{O}{\underset{O}{\overset{\|}{S}}}-CF_3 \quad \xrightarrow{\triangle\!\!\!\!\triangle\,CH_2Cl}$$

$$CF_3-\overset{O}{\underset{O}{\overset{\|}{S}}}-O-(CH_2-\overset{CH_2}{\underset{Cl}{\overset{|}{CH}}}-O)_n-(CH_2)_4-O-(\overset{CH_2}{\underset{Cl}{\overset{|}{CH}}}-CH_2-O)_m-\overset{O}{\underset{O}{\overset{\|}{S}}}-CF_3$$

This system, however, is not a true, classical living polymerization system because there are potential side reactions as shown in figure 1. Side-reactions (a) and (b) would produce trifluorosulfonic acid, which would initiate polymerization of ECH to form PECH having hindered secondary alcohols. Furthermore, reaction by pathway (b) would form double bonds at the ends of the chain, resulting in a decrease in functionality. Side-reactions (c) and (d) would alter the molecular weight and broaden the molecular weight distribution and/or produce nonfunctional cyclic oligomers. Problems associated with side-reaction

(a) were minimized by incorporating small amounts of calcium hydride powder into the polymerization system. Side-reaction (b) may be minimized if the polymerization temperature is kept low. However, it is already clear that the molecular weight is not equal to the monomer/initiator ratio, and the polymers have wide molecular weight distributions (M_w/M_n = 1.4 - 1.5), even when the reaction was carried out in the presence of calcium hydride at 25°C.. Therefore, this polymerization is accompanied by side-reactions. Nevertheless, one can still attain many desired reactions by using highly reactive triflate esters; these are listed below:

(1) Synthesis of telechelic PECH with a much higher molecular weight than 3000 (Table I);

(2) Synthesis of block copolymers (item 7, Table I); and

(3) Capping of the PECH with a variety of nucleophiles (Figure 2).

Capping PECH with appropriate nucleophiles:

ECH was polymerized with BDT at 25 °C for 24 hours, and the reaction mixture was divided into two portions. (a) One was treated with 1,4-butanediol in the presence of a stoichiometric excess calcium hydride, and (b) the other portion was treated with potassium phenoxide.
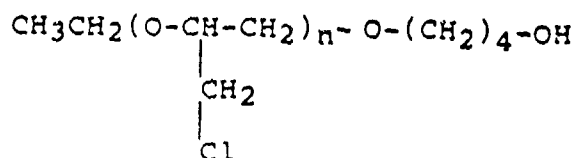
The resulting polymer samples were rigorously purified and characterized.

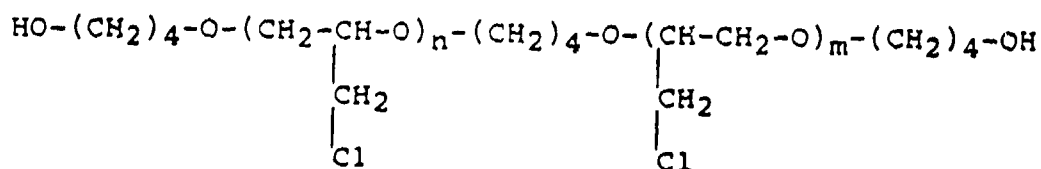## (a) PECH terminated with 1,4-butanediol (PECH-OH)

The end-groups were analyzed by comparing the ^{13}C NMR spectra of PECH and its trifluoroacetate derivative. The peak assignments were made utilizing the spectra of PECH from Minnesota Mining and Manufacturing (3M) and polytetrahydrofuran (PTHF) from duPont, whose end-group structures have been well characterized (Figure 3). These assignments are based on the deshielding effect of hydroxyl groups on neighboring carbons as well as comparing the chemical shift of these carbons when the hydroxy groups are converted to the trifluoroacetate derivatives. The δ-values of the internal carbons of the polymeric chains are not significantly affected by the derivatization, but those of the end groups shift significantly. The general trends in the change of the chemical shifts of the end carbons are such that the α-carbons are strongly deshielded (+ 6ppm), the β-carbons shielded (-3 to -5ppm) and γ- and δ-carbons are slightly shielded when the alcohols are converted to the trifluoroacetate derivatives.

Results of ^{13}C NMR spectra of our PECH-OH and their trifluoroacetate derivatives are shown in figure 4. PECH-OH (I) was

initiated by ET and PECH-OH (II) was initiated by BDT, whose structures are expected to be as follows.

$$CH_3CH_2(O-CH-CH_2)_n-O-(CH_2)_4-OH$$
$$\hspace{3.5cm} |$$
$$\hspace{3.5cm} CH_2$$
$$\hspace{3.5cm} |$$
$$\hspace{3.5cm} Cl$$

PECH-OH (I)

$$HO-(CH_2)_4-O-(CH_2-CH-O)_n-(CH_2)_4-O-(CH-CH_2-O)_m-(CH_2)_4-OH$$
$$\hspace{3.3cm} | \hspace{5cm} |$$
$$\hspace{3.3cm} CH_2 \hspace{4.6cm} CH_2$$
$$\hspace{3.3cm} | \hspace{5cm} |$$
$$\hspace{3.3cm} Cl \hspace{4.8cm} Cl$$

PECH-OH (II)

The chemical shifts for the ethyl carbons at the head of the polymeric chain and the carbons of $-CH_2CH_2CH_2OH$ at the tail, along with the strong multiplet peaks for the internal carbons of PECH-OH (I) are identified along with those of its trifluoroacetate derivative (Figure 4-a). When the alcohols are derivatized the ∂-values of the ethyl carbons (head groups) and the internal carbons of the polymeric chains remain approximately the same. However, the ∂-value changes for the α-C (+5.9ppm), β-C (-4.4 ppm) and γ-C (-1.6 ppm) were observed for the tail group. The shift trend for the peaks of these carbons are similar to those observed for the end-

groups of PTHF. The spectra of PECH (Figure 4-b) initiated by BDT, PECH-OH (II), are the same as those intiated by ET, except the peaks for the ethyl groups in PECH-OH (I) have been replaced by the $-OCH_2CH_2CH_2CH_2O-$ groups present in the middle of the polymer chains.

Additional evidence for PECH-OH (I) and PECH-OH (II) comes from a comparison of the infrared spectra of the alcohol groups. The terminal groups of PECH-OH are similar to those of PTHF; both are primary alcohol groups (Table II). The associated OH-peaks are at 3479 cm^{-1} when the solvent is THF, and 3620 cm^{-1} when the solvent is methylene chloride. These values are close to those of PTHF, and unlike those of secondary alcohols found in 3M PECH. Furthermore, the hydroxyl equivalent weight determinations indicate that PECH-OH (I) is approximately monofunctional and PECH-OH (II) is difunctional (Table III). When the PECH is initiated by BDT and terminated with trimethylol propane, a triol, the polymer becomes tetrafunctional as expected (Table III, item 3).

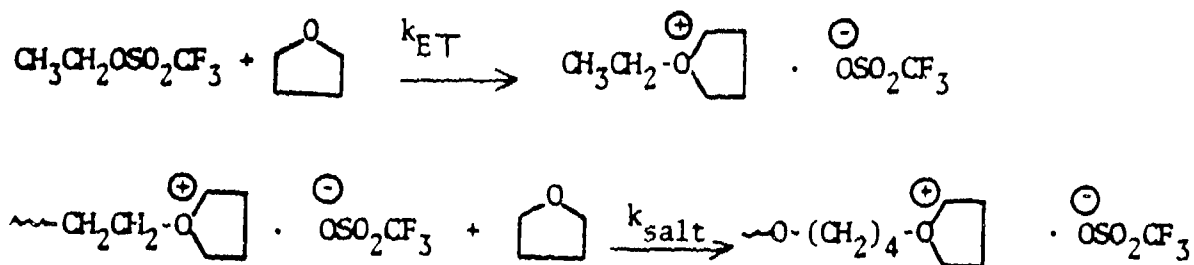**(b) PECH terminated by phenoxy groups (PECH-OPh):**

The end-groups were analyzed by comparing UV and ^{13}C NMR spectra. The UV absorption bands of the phenoxy-terminated PECH are similar to those of methoxybenzene (Figure 5). ^{13}C NMR spectra of the phenoxide

terminated PECH are consistent with the expected structure (Figure 6):

When the spectra of PECH-OH (II) and PECH-OPh are compared, the latter

does not have peaks for the carbons -CH2CH2CH2OH, but has new ^{13}C peaks

at 115, 121, 129.9 and 159.3 ppm. These peaks are assigned to the carbons

of the phenyl ring using n-butylphenylether as a reference.

End-group studies, as described in sections (a) and (b), demonstrate

that treatment of the polymerization reaction mixture with appropriate

nucleophiles gives different end-groups, without altering the PECH

backbone.

Plausible mechanism

Bisoxonium salt, $\left[\begin{array}{c}\oplus\\O\end{array}-(CH_2)_4-O\begin{array}{c}\oplus\\\end{array}\right] \cdot 2CF_3SO_3^{\ominus}$, (BOS) and BDT were

compared in the polymerization of ECH. A detailed kinetic study indicated

that the rate constant for the reaction of THF with a tertiary oxonium salt

was about 200 times greater than THF with ethyl triflate ester[4].

$$CH_3CH_2OSO_2CF_3 + \begin{array}{c}O\\ \square \end{array} \xrightarrow{k_{ET}} CH_3CH_2-O\begin{array}{c}\oplus\\\end{array} \cdot {\ominus}OSO_2CF_3$$

$$\sim CH_2CH_2-O\begin{array}{c}\oplus\\\end{array} \cdot {\ominus}OSO_2CF_3 + \begin{array}{c}O\\ \square \end{array} \xrightarrow{k_{salt}} \sim O-(CH_2)_4-O\begin{array}{c}\oplus\\\end{array} \cdot {\ominus}OSO_2CF_3$$

$$k_{salt}/k_{ET} = 200$$

An experimental study of the polymerization of ECH showed the opposite

effect to that of THF. The bisoxonium salt (BOS) did not produce PECH at

room temperature; even at 40°C, it produced only a 10% polymer

conversion after 24 hours. On the other hand, BDT initiated the

polymerization of ECH at room temperature and produced greater than 50%

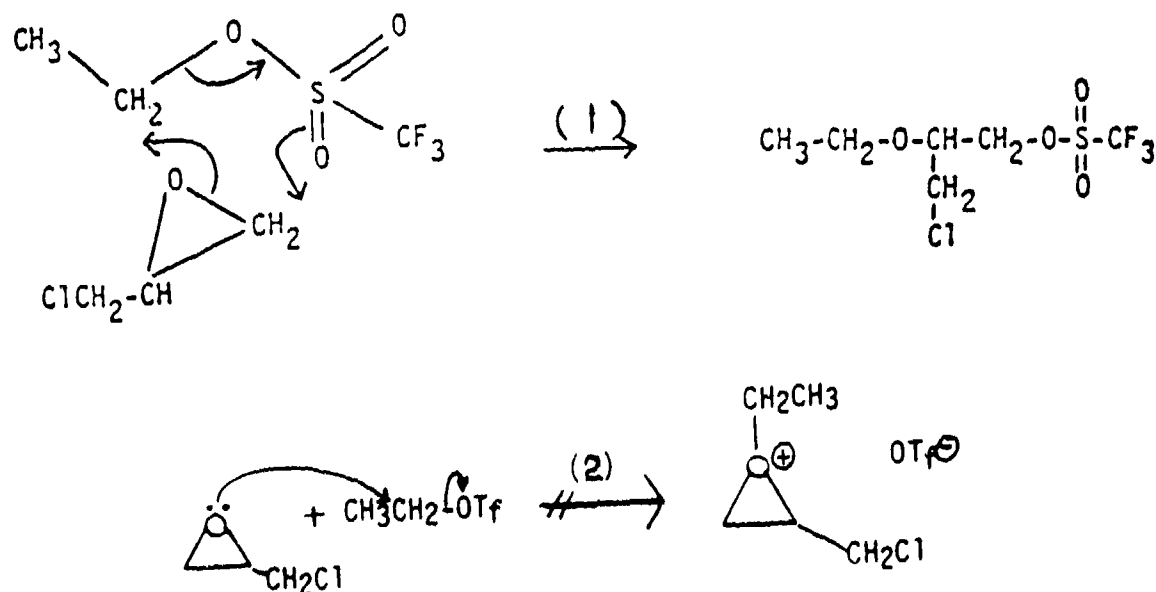polymer conversion after 17 hours (Table IV).
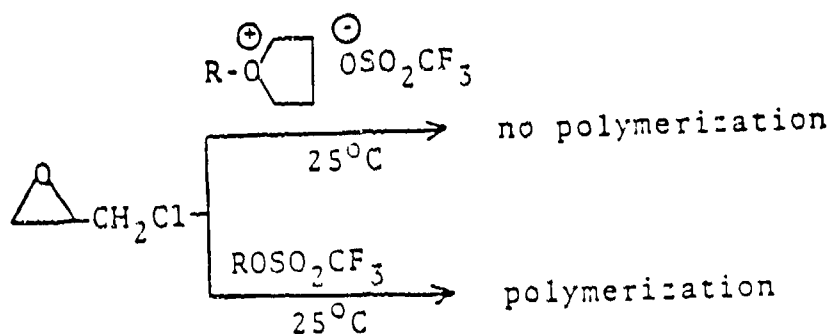
The low reactivity of the oxonium salt (BOS) with ECH may be due to a

high activation energy for the formation of a less stable three-membered

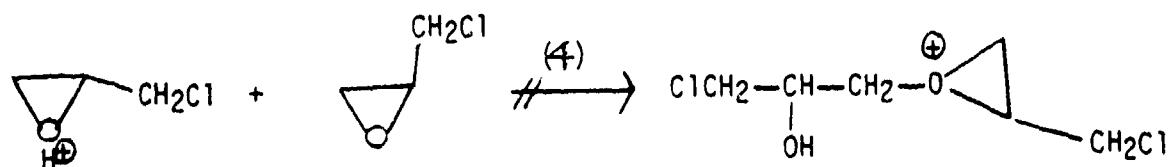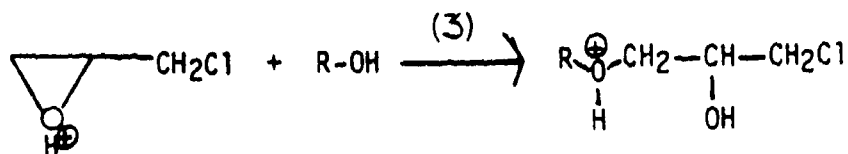ring oxonium ion which has electron withdrawing chloromethyl groups.
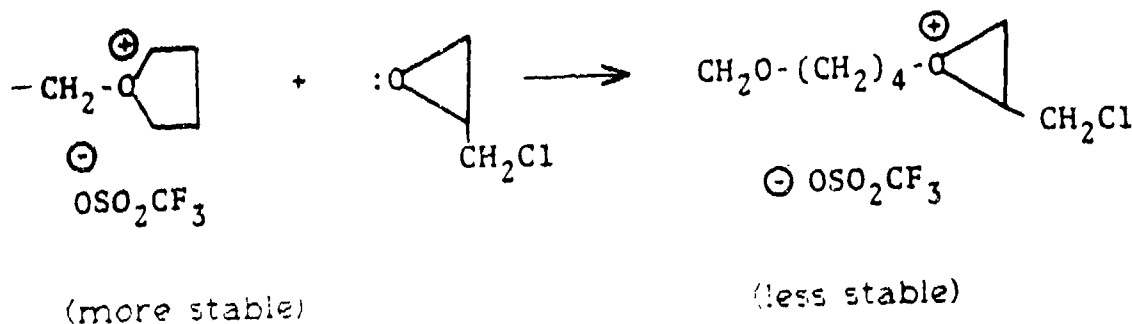
A plausible mechanism for the polymerization of ECH by the

triflates may be a energetically more favorable pathway, such as a cyclic transition state involving six electrons and six orbitals as shown in reaction path (1). A normal nucleophilic substitution reaction such as reaction path (2) would involve a much less stable, partially tertiary oxonium ion as the transition state, and therefore may not be energetically favorable.

$$CH_3-CH_2-O-CH-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-CF_3$$
$$\overset{|}{\underset{|}{CH_2}}$$
$$Cl$$

$$CH_3CH_2-OTf \;\;\xrightarrow{\;(2)\;}\!\!\!\!\!/\!\!\!\!\!\!\longrightarrow$$

Our proposed theory is consistent with the mechanism for the cationic polymerization of ECH described by Okamoto[1] and Penczek[2]: Their experimental results support path (3) rather than path (4) shown below.

$$\text{(epoxide)}-CH_2Cl + R\text{-}OH \xrightarrow{(3)} R\overset{\oplus}{\underset{H}{O}}-CH_2-\underset{OH}{CH}-CH_2Cl$$

$$\text{(epoxide)}-CH_2Cl + \text{(epoxide with }CH_2Cl) \xmapsto{(4)} ClCH_2-\underset{OH}{CH}-CH_2-\overset{\oplus}{O}\text{(epoxide)}-CH_2Cl$$

A pericyclic type reaction involving sulfonate esters has not been reported in the literature. Hence, this type of polymerization should be investigated further. Studies such as side-reaction products, effect of solvent polarity, kinetics of polymerization, and correlation of molecular weight with polymer conversion are currently underway.

EXPERIMENTAL SECTION

Monomer:

The monomer, epichlorohydrin, was purchased from Aldrich Chemical Co. and distilled from calcium hydride under a nitrogen atmosphere.

Solvents:

THF and dioxane were distilled from lithium aluminum hydride, under a nitrogen atmosphere, and dichloromethane was distilled from calcium hydride.

Initiators:

(1)   Ethyl triflate (ET)

Ethyl triflate, 99% purity, was purchased from Aldrich Chemical Co. and used without further purification.

(2)   1,4-Butaneditriflate (BDT)

BDT was synthesized from THF and trifluoromethoanesulfonic anhydride (purchased from Aldrich Chemical Co. and used without further purification), using the following procedure.

To a flame dried, argon flushed, 500 mL three-necked flask equipped with a 50 mL addition funnel, thermometer, argon inlet tube and a magnetic stirring bar, was added 150 mL of dichloromethane, 1.0 g (0.024 moles) calcium hydride powder and 100 g (0.354 mole) of trifluoromethansulfonic anhydride. The solution was stirred at 0°C while adding 30.7 g (0.425 mole) THF dropwise. After the addition, the reaction mixture was allowed to warm to room temperature and stirred for an additional 30 minutes. The reaction mixture was subjected to a rotary vacuum, at 35 °C, for an hour to remove excess THF . The remaining residue was dissolved in a minimum amount of dichloromethane, filtered through a medium frit, sintered glass funnel. The solution was concentrated by blowing of the excess dichloromethane with a stream of

argon. The slightly turbid solution was stored in the freezer overnight.

The crude product, off-white crystals, were collected by a suction

filtration while the solution was cold, and then recrystallized from

dichloromethane, yielding 83.7g (84%). The entire filtration and

recrystallization processes were carried out in a dry box. The purified

product was colorless crystals, m.p. 35-36 $^{\circ}$C, purity 98% (based on

GPC). Analysis: calculated for $C_6H_8F_6O_6S_2$: C 20.3, H 2.3, F 32.2, S 18.1;

determined: C 19.85, H 2.42, F 32.20, S 18.00. Proton NMR in C_6D_6: ∂ 3.73

(4H, m) and 1.01ppm (4H, q). IR in CCl_4: 1427, 1220, 1146 and 920 cm^{-1}.

(3)   Bisoxonium triflate (BOS)

The synthetic procedure of Smith[5] was used.

Polymerization of ECH

Polymerization of ECH, using BDT as the initiator, is described here

as an example. All other polymerization procedures are the same except

for variations of initiator, monomer to initiator ratio, and the reaction

conditions. A 250 mL single-neck flask with 0.228 g (0.011 equivalents)

calcium hydride, was flame dried and cooled under nitrogen atmosphere.

To the cooled flask were added 3.83g (0.0216 equivalents) of BDT, 10 g

(0.10 equivalents) of dichloromethane and 20.0 g (0.216 equivalents) ECH.

Argon was bubbled through the reaction mixture for five minutes and the

reaction flask was placed in a 25 °C oil bath equipped with an automatic

shaker, and allowed to shake for 24 hours under an argon atmosphere. The

reaction mixture was then treated with the desired terminating agent.

Termination Reaction of PECH:

The polymerization mixture was filtered to remove calcium hydride,

and the filtrate was slowly added to a stirred solution of the appropriate

terminating agent, in a nitrogen atmosphere. The resulting mixture was

placed in a 30 °C oil bath, equipped with an automatic shaker, and shaken

for one to three days. It is important that the terminating agent is

soluble in the PECH solution, otherwise a complete termination reaction is

difficult to achieve. A trace of unreacted triflate ester causes a slow

degradation of the polymer. Dioxane was found to be the best co-solvent.

The terminating agents, (1) potassium phenoxide, (2) calcium or lithium

alkoxide, and (3) aqueous potassium carbonate, in the amounts of a ten-

fold the stoichiometric excess based on the BDT, were used.

(1) Potassium phenoxide was synthesized by dissolving 92.2g (0.98

moles) of phenol in a saturated aqueous solution of 50.0g (0.89 moles)

potassium hydroxide, followed by evaporation of water and the residue

was given a final drying in a vacuum oven, over P_2O_5. Potassium

phenoxide was purified by recrystallization from anhydrous dioxane. m.p.

112-113 °C, equivalent weight by acid titration: 136g/eq (theoretical 132

g/eq). Purified potassium phenoxide, 4.3g, was dissolved in 60g dioxane

and used in the terminating reaction.

(2) Calcium hydride, 2.27g (0.108 equivalents), was added to a

solution of 9.74g (0.216 equivalents) of 1,4-butanediol (vacuum distilled

from calcium hydride) in 29.2g anhydrous dioxane and used as a

terminating agent.

(3) A one to one volumetric ratio of 10% aqueous potassium

carbonate solution and dioxane was used as a terminating agent.

Purification (fractionation) of terminated PECH

The method used varied depending on the terminating agent used. The

following general procedure is illustrative of the method used to purify

the terminated PECH. The mixture was filtered if solids were present, and

the organic layer (polymer solution) was separated if there were two

layers. The polymer solution was washed with water until the wash water

was neutral and the solvent was removed using a rotary evaporator at 40-

45 °C. The residual polymer was washed three times with cold methanol.

The polymer was then dissolved in a minimum amount of toluene followed by rotary evaporation of this solution using the vacuum of an oil pump at 50 °C until its weight remained constant. The substantial removal of methanol was assured by GPC and NMR analyses. It is critical that methanol was removed as completely as possible; otherwise a false equivalent weight determination and more importantly a poor rubber network formation would occur due to the chain terminating reaction by methanol.

Polymer Characterization:

(1) Average molecular weight and polydispersity were determined by gel permeation chromatography (GPC) using THF as the eluent and PECH standards (Polysciences) and polystyrene standards (Pressure Chemicals). The GPC instrumentation was a Waters HPLC system consisting of a M730 module, 6000A pump, R401 refractive index detector, and 100, 1000 and 5000 angstrom ultrastyragel columns connected in series.

(2) Hydroxy Equivalent weight of PECH was determined by two methods, which were compared: Method (a) A physical method where PECH was dissolved in THF and the THF-associated OH peak was monitoted by infrared spectroscopy[6]; and Method (b) A physical chemical method in which PECH was allowed to react with excess p-

toluenesulfonyl isocyanate (TSNCO) and the absorbance of the

resulting urethane peak was monitored. The second method is a

modification of a chemical method developed by Thiokol (Procedure

D385, Revision A, 1981). Both methods gave the same values within

experimental error (5%), and the reported values are their average

values. A Perkin-Elmer, model 1800 FTIR spectrometer, with a 1.0 mm

barium fluoride cell was used for Method (a) and a 0.2 mm sodium chloride

cell was used in Method (b). Two calibration standards, 1-octanol and

hydroxypropyl acrylate were used in method (a), and the procedure used

has been descirbed in detail[6]. Method (b): Calibration samples were

prepared using a clean, dry 10 mL volumetric flask which was half-filled

with dichloroethane (DCE), stoppered, and tared on the balance. The

appropriate amount (0.2 to 0.6 meq.) of 1-octanol, the calibration

standard, was then injected into the flask with a microliter syringe. After

re-taring, five drops (0.07g) of 10% w/w ferric acetylacetonate catalyst

(FeAA) were added. After taring once more, enough stock solution of 10%

v/v TSNCO (purchased from Aldrich and used as is) in DCE to provide a four

fold excess of the isocyante was added dropwise. The flask was then

adjusted to the mark with DCE, shaken thoroughly, and the FTIR spectrum

of the sample was taken as soon as possible. The urethane absorbance at

1753 cm^{-1} was monitored at 25 ^{0}C. The urethane reaction is usually complete in three minutes. A linear Beer's Law plot, intercepting near zero, having the calibration equation below, was obtainend.

meq/L OH = (69.39 0.46)A, where A is the absorbance.

Polymer samples were run in a manner similar to those of 1-octanol except a 5 ml volumetric flask was used. The more hindered alcohols such as 3M PECH samples required almost 20 minutes for the completion of the urethane reaction.

REFERENCES

1. Y. Okamoto, ACS Polymer Preprints 25, No. 1, 264-265 (1984)

2. Y. Okamoto, "Ring Opening Polymerization: Kinetics, Mechanisms and Synthesis", edited by J. E. McGrath, ACS Symposium Series, 286, 361-372 (1984)

3. S. Penczek, ACS Polymer Preprints, 29, No. 2, 38-40 (1988)

4. K. Matyjaszewski, T. Diem, and S. Penczek, Macromol. Chem. 180, 1817-1819 (1979)

5. S. Smith and A. J. Hubin, ACS Polymer Preprints, 13, No. 1, 66-71 (1972)

6. C.S.Y. Kim, A.L. Dodge, S. Lau, and A. Kawasaki, Anal. Chem. 54, 232-238 (1982).

II. Characterization of PECH and the Kinetics of Urethane Formation

PECH was synthesized using BDT as the initiator, as described in Section I, and terminated with various terminating agents. Chemical equations for the termination reactions are shown in Figure 2, Section I. These PECH samples were characterized in terms of average molecular weight, polydispersity, OH-equivalent weight, functionality and the relative reactivity with isocyanates for the urethane formation.

Characterization of PECH

Table V lists the expected structures for the end groups for each terminating agent along with the experimental values of number average molecular weight (M_n) and equivalent weight (EW). The functionality of polymer samples was estimated from the relationship, $f_c = M_n/EW$. Effective functionalities (f_e) of difunctional polymers were also determined[1], and the results were verified by a cure study. All the "difunctional polymers" including 3M PECH have the functionality values of less than 2.0, indicating that there are some unfavorable side reactions occurring during the polymerization. Expected side reactions were discussed in Section I (Figure 1).

One of the methods to assure that PECH undergoes proper cure reactions with isocyanates and thus develop effective network structures, would be to synthesize PECH having functionalities greater than 2.0. This can be achieved by terminating PECH with a triol, such as Isonol and trimethylol propane (Items 4 & 5, Table V). These PECH samples should have functionality values close to 4.0, and the cure study indicated a very tight network formation after the sample was cured.

Kinetics of Urethane Foromation

One of the factors influencing the effective binder network formation is the possibility of competing side-reactions during the cure. Undesirable side reactions should be minimized. Side-reactions become more prevalent when the binder is highly plasticized and/or the binder components have nitrato, nitro, or azido groups. One way to minimize the competing side-reactions would be to make the polymeric alcohols more reactive. For example, reactive primary alcohol groups, such as -CH2CH2CH2OH, should be more desirable than the less reactive, hindered secondary alcohol groups, which are present in 3M PECH.

The advantage of our newly developed synthetic procedure is that it produces PECH with variable molecular weights (Table I, SectionI), but it also gives the versatility of producing PECH with alcohol groups having different reactivity with isocyanates.

The results of the kinetic study are summarized in Figures 7 and 8 and are consistent with those expected. PECH terminated with 1,4-butanediol gives end-group structures identical to poly-THF and is expected to be the most reactive of the PECH diols. PECH terminated with water should also have primary alcohols, however these should be sterically hindered at the β-carbons. 3M PECH has highly hindered secondary alcohols and is expected to be the least reactive of the three diols (Compare items 1, 2 &3. Table V). When the tetrafunctional PECH are compared, the results are also as expected (Figure 8). The PECH terminated with trimethylol propane is expected to be less reactive than the one terminated with Isonol because the alcohol groups are more s terically hindered. The kinetic results show that the ones terminated with Isonol are the most reactive and 3M PECH is least reactive.

EXPERIMENTAL

Characterization Methods:

Effective functionalities of PECH diols were determined by the procedure described previously[1]. The other methods are described in Section I.

Kinetic Study:

All infrared spectra were obtained using a Perkin-Elmer model 1800 FTIR spectrometer (quantitative mode, 4 cm^{-1} resolution.) Urethane

reactions were run in a Spectra-Tech model HT-32 variable temperature cell with NaCl windows and a 0.20 mm path length. Cell temperature was controlled to $\pm$ 0.2º C for runs of four hours duration ands $\pm$ 0.4º C for 24-hour runs, with an Omega model CN-5002 proportional controller. Reaction times were obtained by accessing the clock in the computer which was controlling the FTIR for each spectrum acquired.

All volumetric glassware and microliter syringes were rigorously cleaned and dried before use. A 10-ml volumetric flask was tared and sufficient prepolymer for 60 meq/L OH concentration was added. The prepolymer was dissolved in dichloroethane (DCE), and a measured amount of 10% w/w catalyst in DCE was added using a 50 microliter syringe. The concentration of catalyst (ferric acetylacetonate) in the final solutions was 147 mg/L. The solution was brought to the mark and then used to fill a clean, dry 5-mL volumetric flask to its mark. A portion of the remaining solution was placed in the clean, dry infrared cell, and its spectrum at 41º C was acquired and stored. The reaction was initiated by using another 50 micro-liter syringe to add 0.035 g of n-butyl isocyanate to the prepolymer solution in the 5-ml flask. The reaction mixture was then placed in the infrared cell and, as soon as the temperature reached 41º C, the FTIR was programmed to take a series of spectra at specified time intervals. Each spectrum was stored for later analysis, after first subtracting the background of the prepolymer-catalyst spectrum which had been stored earlier. In each run, data were acquired through the end of the third isocyanate half-life. One final spectrum was aquired after an overnight reaction (18 to 48 hours after reaction was started.)

REFERENCES

1. C. S. Y. Kim, Final Technical Report, AFRPL TR-83-002, 67-68 (1983)

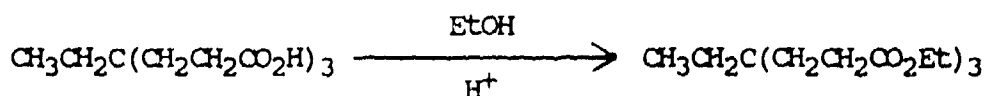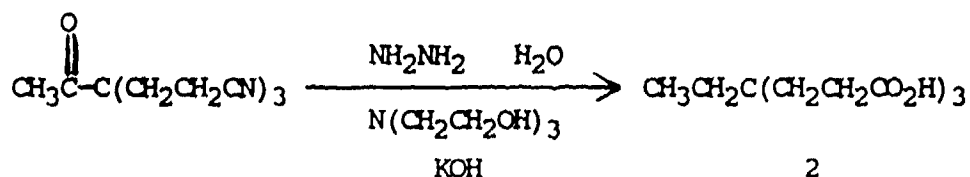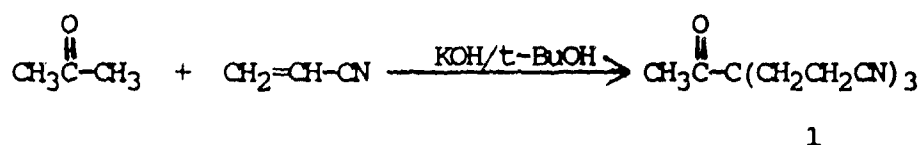III. **Polyfunctional Triflates: Syntheses of Precursors**

The objective of this study was to synthesize compounds with three or four primary alcohol groups in the same molecule. Further requirements are that there be more than three carbon atoms between alcohol groups to avoid the problems of steric hindrance. The alcohols could then be converted to triflate esters which may be used as initiators for the synthesis of polyfunctional epichlorohydrin polymers. Synthesis and the evaluation of these triflate esters, as the initiators, are planned in the future.

The method chosen for the synthesis of these polyols was the reduction of the appropriate polycarboxylic acid ester with lithium aluminum hydride. Two tricarboxylic acids and one tetracarboxylic acid were used as starting materials. One of the two tricarboxylic acids, 1,3,5-pentanetricarboxylic acid, is commercially available[1] as the anhydride. The other, 1,1,1-tris (2-carboxyethyl) propane was synthesized in this study. The tetracarboxylic acid, 1,2,3,4-butanetetracarboxylic acid is also commercially available.

Synthesis of aliphatic triols and tetraols, where the alcohol groups are primary and not attached to a neopentyl carbon atom, are best accomplished by the reduction of the appropriate polycarboxylic acid ester. At first, it was thought that the tri- and tetra-carboxylic acids could be obtained from the readily available 2-hydroxymethyl-2-methyl-1,3-propanediol and pentaerythritol respectively. This could be accomplished by synthesizing the corresponding alkyl halides and reacting these compounds with cyanide ion. Hydrolysis of the resulting polynitrile compounds should give the polycarboxylic acids. This was attempted, but it was found that the neopentyl alkyl halide intermediates are very resistant to displacement by cyanide ion. The reaction was attempted using various solvents and with bromide or tosylate as the

leaving group. However, in each case, only starting material was recovered. Hexamethylphosphoramide (HMPA) has been suggested as being an excellent solvent for displacement reactions involving neopentyl structures[2]. This solvent was not used in this study because of its high toxicity and expense.

It was decided that 1,3,5-pentanetricarboxylic acid would be a suitable starting material for the synthesis of the triol. Esterification with ethanol, followed by reduction with lithium aluminum hydride, gave 4-hydroxymethyl-1,7-heptanediol in 67% yield overall. Although this compound contains no alcohol groups attached to a neopentyl carbon atom, it was felt that the hydroxymethyl group, when converted to the triflate ester, would be too sterically hindered and cause problems during the initiation reactions with epichlorohydrin. With this consideration, a new triol was synthesized that contained no hydroxymethyl groups. This was accomplished with acetone and acrylonitrile as the starting materials, using the following sequence of reactions:

$$CH_3\overset{O}{\overset{\|}{C}}-CH_3 \;+\; CH_2=CH-CN \;\xrightarrow{KOH/t-BuOH}\; CH_3\overset{O}{\overset{\|}{C}}-C(CH_2CH_2CN)_3$$

1

$$CH_3\overset{O}{\overset{\|}{C}}-C(CH_2CH_2CN)_3 \;\xrightarrow[\substack{N(CH_2CH_2OH)_3 \\ KOH}]{NH_2NH_2 \quad H_2O}\; CH_3CH_2C(CH_2CH_2CO_2H)_3$$

2

$$CH_3CH_2C(CH_2CH_2CO_2H)_3 \;\xrightarrow[H^+]{EtOH}\; CH_3CH_2C(CH_2CH_2CO_2Et)_3$$

$$CH_3CH_2C(CH_2CH_2CO_2Et)_3 \;\xrightarrow{LiAlH_4}\; CH_3CH_2C(CH_2CH_2CH_2OH)_3$$

The reaction of acrylonitrile with acetone was carried out using the procedure described by Bruson[3]. The synthesis of 2 was reported by Fliedner[4]. In Fliedner's studies, 2 was obtained by the Wolff-Kishner reduction of the tricarboxylic acid derivative of 1. It was discovered in this study that the reduction of the ketone and the hydrolysis of the nitrile groups could be carried out in the same reaction flask, to give good yields of 2. Initially this reaction was attempted using diethylene glycol as the solvent, but this failed because it was not possible to separate the product from the solvent. The reaction was then carried out using triethanolamine as the solvent[5]. Acidification of the solvent, with concentrated hydrochloric acid, allowed the product to be isolated in an 82% yield. This tricarboxylic acid was esterified with ethanol, in toluene, to give the tri-ethyl ester. Reduction of the ester with lithium aluminum hydride, in tetrahydrofuran, gave 1,1,1-tris-(3-hydroxypropyl)-propane in 79% yield.

The tetraol was synthesized by esterifying 1,2,3,4-butanetetracarboxylic acid with ethanol followed by reduction of this ester with LiAlH$_4$. This procedure gave 3,4-bis-(hydroxymethyl)-1,6-hexanediol in an overall yield of 68%. This tetraol was soluble only in the more polar solvents, such as ethanol. The insolubility in nonpolar solvents proved to be a problem during the initiator studies. It was decided that this problem could be eliminated if the tetraol could be converted to 3,3'-bis-tetrahydrofuran since it was known that tetrahydrofuran can be converted to the di-triflate by reaction with triflic anhydride. Reaction of 3,3'-bis-tetrahydrofuran with triflic anhydride should therefore give the tetratriflate. The synthesis of 3,3'-bis-tetrahydrofuran was reported by Buchta[6]. In that work the compound was formed by reacting 3,4-bis-hydroxymethyl-1,6-hexanediol with potassium bisulfate at

180-190°. Since no other details of the reaction were given, it was decided that another procedure should be used to synthesize bis-tetrahydrofuran. The procedure selected was described by Rice[7], for the preparation of 3,9-bis-Dioxaspiro [5.5] undecane. Following Rice's procedure, 3,4-bis-hydroxymethyl-1,6-hexanediol was heated in 80% sulfuric acid for 3 hours, at 100°, to give 3,3'-bis-tetrahydrofuran in 65% yield. At this temperature, significant charring also occurred. When the reaction was carried out at 85°, the yield of distilled product was increased to 86% and with very little charring.

EXPERIMENTAL

4-Acetyl-4-(2-cyanoethyl)-heptanedinitrile

To a solution of 320g of t-butanol, 116.2g of acetone and 10g of 30% methanolic potassium hydroxide was added, dropwise, 318.4g of acrylonitrile. The mixture was vigorously stirred while maintaining the temperature between 0° and 5° with an ice-salt bath. Stirring became very difficult, near the end of the acrylonitrile addition, because the product had precipitated out. The mixture was stirred an additional 2 hours, at 5°, after all the acrylonitrile was added. The reaction mixture was then made weakly acidic with a 10% HCl solution. The product was filtered, washed with water, then with THF and finally dried overnight at 60°. The yield of crude product was 334g (77%). Recrystallization from acetone, containing a small amount of water to clarify the solution, gave 245g (3 crops) of colorless crystals; m.p. 154° (lit.[3] m.p. 154°). Anal. Calc'd. for $C_{12}H_{15}N_3O$: C, 66.33; H, 6.96; N, 19.34 Found: C, 66.48; H, 6.88; N, 19.29.

4-(2-Carboxymethyl)-4-ethyl-1,7-heptanedioic acid

In a four liter, three-necked flask were placed 800g of triethanolamine, 273.7g of potassium hydroxide, 105.14g of hydrazine monohydrate, 95 mL of water and 152.1g of finely powered 4-acetyl-4-(2-cyanoethyl)-heptanedinitrile. The mixture, which became homogeneous as it was warmed, was stirred for 2 hours at 100°. Ammonia began to evolve at this temperature. The mixture was refluxed an additional 2 hours at 138°. Excess hydrazine and water were codistilled until the temperature reached 195°. The mixture was allowed to reflux for an additional 2 hours at 195-200°. The contents were poured, while still hot, into a four liter beaker and cooled to 40°. The mixture was slowly acidified with concentrated HCl to a pH of 3.5-4.0, then cooled to 0° and filtered. The solid, which consisted of product and triethanolammonium chloride, was dried at 60° for 16 hours then extracted with acetone to give 138g (77%) of the crude acid. The product was recrystallized from water to give 130g of the pure tri-acid; m.p. 162.5-163° (lit[4]. m.p. 160-161°). Anal. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75 Found: C, 55.37; H, 7.75.

1,1,1-Tris-(3-hydroxypropyl)-propane

A mixture of 26.03g of 4-(2-carboxyethyl)-4-ethyl-1,7-heptanedioic acid, 75g of ethanol, 1g of concentrated sulfuric acid and 30 mL of toluene was refluxed for 24 hours. The distillate, which was collected in a Dean-Stark trap, was removed periodically and swirled with anhydrous magnesium sulfate to remove the water and filtered back into the reaction mixture. The excess ethanol and toluene were then distilled off, as completely as possible. The contents of the flask were then placed in a separatory funnel and the reaction flask rinsed with chloroform which was also added to the separatory funnel.

The mixture was washed with 200 mL of water containing 1.5g of sodium carbonate, followed by 200 mL of water. The chloroform solution was dried with magnesium sulfate, filtered and the solvents removed with a rotary evaporator. Distillation of the crude ester at, 140-142° at 0.12 mm, gave 30g (88%) of pure product.

A solution of 29.27g of the tri-ester in 75 mL of dry THF was added dropwise to 10.19g of lithium aluminum hydride in 300 mL of dry THF. The addition rate was adjusted to maintain the reaction temperature at approximately 40°. The mixture was allowed to stir for 1 hour at room temperature, after the addition was complete. The excess $LiAlH_4$ was then decomposed by slowly adding 10.19 mL of water, followed by 10.19 mL of a 15% sodium hydroxide solution and 30.6 mL of water. The solid was filtered and washed with 200 mL of THF. The THF was removed by distillation and the crude triol was distilled, 166° at 0.08 mm, to give 14.6g (79%) of the pure product. The product solidified, after standing at room temperature, to give a crystalline solid, m.p. 71-72.5°.

Tetraethyl-1,2,3,4-butanetetracarboxylate

The procedure for the preparation of this ester is the same as that described above, using 1,2,3,4-butanetetracarboxylic acid (118.26g, 99%) 320g of ethanol, 200 mL toluene and 2.1g of concentrated sulfuric acid. The ester distilled at 169-171° (0.05 mm) to give 132g (76%).

3,4-Bis-hydroxymethyl-1,6-hexanediol

Tetraethyl-1,2,3,4-butanetetracarboxylate (69.28g) in 200 mL of THF was added to a suspension of 31.96g of lithium aluminum hydride (95%) in 400 mL THF. The rate of addition was adjusted to maintain the temperature between 55–60°. The mixture was then stirred at 55–60° for five hours. The mixture was cooled to 10° and 32 mL of water was slowly added, followed by 32 mL of 15% sodium hydroxide and 96 mL of water. The solids were filtered, washed with THF and extracted with 300 mL of ethanol. The ethanol and THF solutions were combined and evaporated to dryness. Water was added to the resulting dry material and the solution was neutralized with dilute sulfuric acid. The water was evaporated and the solid extracted with ethanol, to remove the product from the sulfate salts. Recrystallization from the ethanol/THF gave 32g (90%) of the pure tetraol; m.p. 90–91°.

3,3'-Bis-tetrahydrofuran

3,4-Bis-hydroxymethyl-1,6-hexanediol (12.98g) and 50 mL of 80% sulfuric acid were placed in a 100 mL three-necked flask. The mixture was heated to 100° for 3 hours, then cooled to 25°, poured into 100 mL of water and neutralized with potassium carbonate. The solution was extracted with two-200 mL portions of diethyl ether. The ether solution was dried over magnesium sulfate and then filtered. Evaporation of the ether gave 9.3g (90%) of the crude product. Distillation at, 80° at 4 mm, gave 6.7g of the pure 3,3'-bis-tetrahydrofuran.

REFERENCES

1. Kay Fries, 10-T Link Dr., Rockleigh, N.J., 07647.

2. B. Stephenson et. al., J. Am. Chem. Soc., **94**, 4184-4188, (1972).

3. H. A. Bruson, J. Am. Chem. Soc., **64**, 2850-2858, (1942).

4. L. J. Fliedner and I. J. Pachter, (Endo Laboratories, Inc.)
   U.S. Pat. 3,929,887.

5. P. D. Gardner et. al., J. Am. Chem. Soc., **78**, 3425-3427, (1956).

6. E. Buchta and K. Greiner, Naturwissenschaften, **46**, 532, (1959).

7. L. M. Rice and K. R. Scott, J. Org. Chem., **32**, 1966-1970, (1966).

TABLE I

Polymerization of ECH Under Various Conditions

Item	Initiator (I)	[I]/[M]*1	Rexn Temp^{o}C/Time, hr	% Yield*2	M_n(GPC)*3
(1)	ET	1/10	40/17	35	3,400
(2)	ET	1/20	40/17	35	7,000
(3)	BDT	1/10	40/17	40	6.400
(4)	BDT	1/10	25/24	50	6,900
(5)	BDT	1/20	25/17	50	15,000
(6)	BDT	1/20*4	25/48	--	14,000
(7)	BDT	1/20*5	25/48	--	13,000

*1 [I]/[M] = equivalent ratio

*2 yield after purification

*3 Number Average Molecule Weight of purified (fractionated) PECH
    (GPC using PECH standards as reference in THF)

*4 50% of monomer was added at the beginning of the reaction and
    the remainder was added 24 hours later.

*5 50% of monomer for the first 24 hours was ECH. The other half of
    the monomer was THF which was added 24 hours later.

TABLE II

Associated OH Bands of PECH (40 meq/L)

End Groups	THF Solution λmax, cm^{-1}	CH$_2$Cl$_2$ Solution λmax, cm^{-1}
PTHF $-O-CH_2CH_2CH_2CH_2OH$	3480	3618
3M PECH $-O-CH_2-CH-OH$ $\quad\quad\quad\; CH_2Cl$	3409	3571
(PECH-OH)*1 $O-CH-CH_2-OCH_2CH_2CH_2CH_2OH$ $\quad CH_2Cl$	3479	3620
(PECH-OH)*2 $-O-CH-CH_2OCH_2CH_2CH_2CH_2OH$ $\quad\quad CH_2Cl$	3473	3620

*1 PECH initiated with ET.

*2 PECH initiated with BDT.

TABLE III

Number Average Molecular Weight and Equivalent Weight of PECH
(Polymerization for 17 hours at 40°C in dichloroethane)

Item	Initiator	I / M [1]	Terminating Agent	M_n [4]	M_w/M_n	OH-Eq. Wt.
(1)	ET	1/10	BD[2]	3400	1.4	3610
(2)	BDT	1/10	BD	6400	1.5	3340
(3)	BDT	1/10	TMP[3]	6400	1.5	1670

[1] I / M = equivalent ratio.

[2] 1,4-butanediol

[3] trimethylol propane

[4] number average molecular weight by GPC using PECH standards
     as reference in THF

TABLE IV

Polymerization of ECH ($[I]/[M]^{*1} = 1/20$)

Item	Initiator (I)	Rexn Temp°C/Time, hr	%Yield[*2]	M_n[*3]
(1)	BOS	20/24	0	--
(2)	BOS	40/24	10	7,500
(3)	BOS	70/24	50	7,000
(4)	BDT	25/17	50	15,000

*1 equivalent ratio.
*2 yield after purification.
*3 number average molecular weight by GPC using PECH standards
as reference in THF.

TABLE V

PECH With Different End-Groups

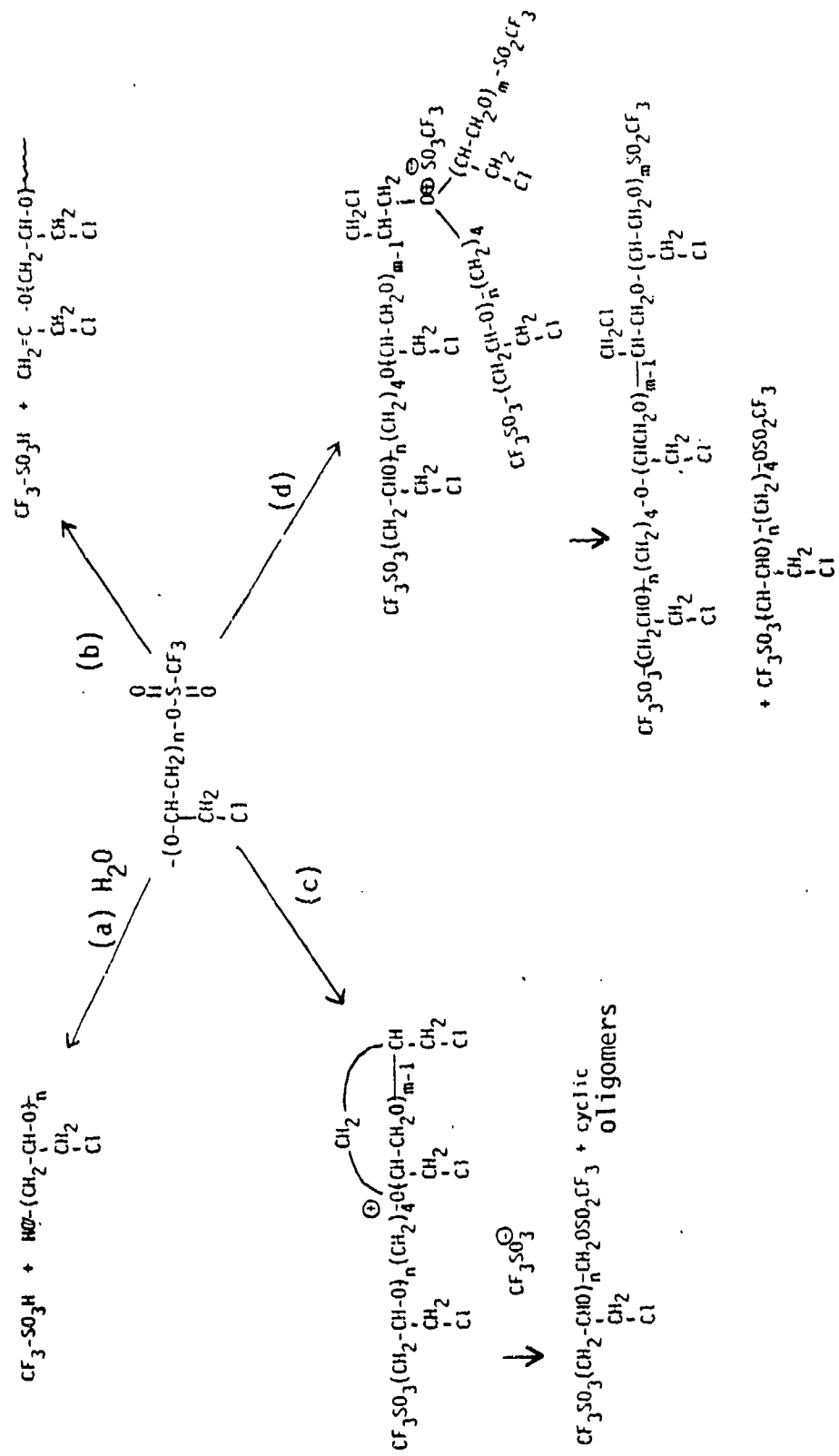| PECH	Terminating Agent	Expected Structure	M_n (M_w/M_n)	E.W.	fc	fe	cure
(1) 3M	—	$-CH_2-CH-OH$ CH_2Cl	2500	1300	1.92	1.75	boardline
(2) LK-8	$HO-(CH_2)_4OH$ CaH_2	$-OCH_2CH_2CH_2CH_2OH$	6400 (1.5)	3340	1.92	1.70	partially
(3) LK-9	K_2CO_3/H_2O	$-O-CH-CH_2OH$ CH_2 Cl	6400 (1.5)	3340	1.92	1.70	partially
(4) LK-15	$CH_3CH_2C(CH_2-O-CH_2CH_2OH)_3$ (Isonol)	$-OCH_2CH_2OH$	6400 (1.5)	1660	3.85	--	Yes
(5) LK-16	$CH_3CH_2C(CH_2OH)_3$	$-OCH_2-C-CH_2OH$ CH_2CH_3 CH_2 OH	6400 (1.5)	1670	3.83	--	Yes

Figure 1. Possible Side Reactions During ECH Polymerization With BDT

Starting material (left, vertical):

$F_3CO_2S-(O-CH_2-CH)_n-O-(CH_2)_4-O-(CH-CH_2-O)_m-SO_2CF_3$
with CH_2Cl substituents

(a) H_2O / base →
$HO-(CH_2-CH-O)_n-(CH_2)_4-O-(CH-CH_2-O)_m-H$
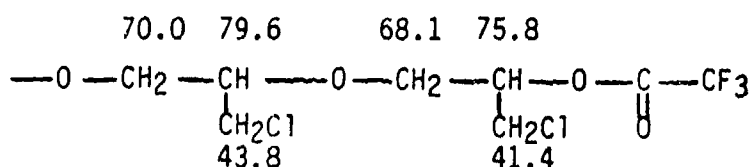with CH_2Cl branches

(b) $HO-(CH_2)_4-OH$ / base →
$HO(CH_2)_4-O-(CH_2-CH-O)_n-(CH_2)_4-O-(CH-CH_2-O)_m-(CH_2)_4OH$
with CH_2Cl branches

(c) $HO-CH_2-CH-(CH_2)_4OH$ (with OH) / base →
$HO-CH_2-CH(CH_2)_4O-(CH_2CH-O)_n(CH_2)_4O-(CH-CH_2O)_m-(CH_2)_4-CH-CH_2OH$
with OH and CH_2Cl branches

(d) $\bigcirc-ONa$ →
$\bigcirc-O-(CH_2-CH-O)_n(CH_2)_4-O-(CH-CH_2O)_m-\bigcirc$
with CH_2Cl branches

(e) RSH / base →
$R-S-(CH_2-CHO)_n(CH_2)_4O-(CH-CH_2)_m-SR$
with CH_2Cl branches

(f) R_2NH →
$R_2N-(CH_2-CHO)_n(CH_2)_4-O-(CH-CH_2)_m-NR_2$
with CH_2Cl branches

Figure 2. Various Termination Reaction of PECH

(a) PECH Model:
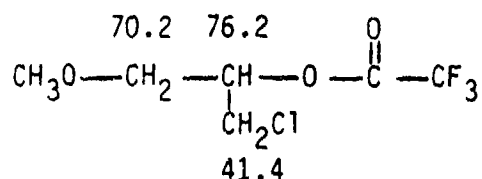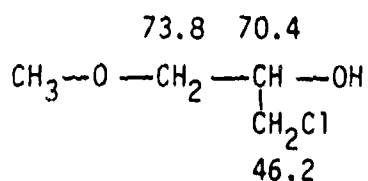
73.8 70.4
$CH_3-O-CH_2-CH-OH$
|
CH_2Cl
46.2

70.2 76.2
$CH_3O-CH_2-CH-O-C-CF_3$ (C=O)
|
CH_2Cl
41.4

($\triangle$ ppm): α-CH (+5.8), β-CH$_2$ (-2.6), β-CH$_2$Cl (-4.8)

(b) 3M PECH:

70.0 79.6   70.1 69.8
$-O-CH_2-CH_2--O-CH_2-CH-OH$
| |
CH_2Cl CH_2Cl
43.8   45.3

70.0 79.6   68.1 75.8
$-O-CH_2-CH--O-CH_2-CH-O-C-CF_3$
| | (C=O)
CH_2Cl CH_2Cl
43.8   41.4

($\triangle$ ppm): α-CH (+6.0), β-CH$_2$ (-2.0), β-CH$_2$Cl (-3.9)

(c) Teracol: 27.1 70.8   70.9 27.1 30.4 62.4
$-O-CH_2-CH_2-CH_2-CH_2-O-CH_2-CH_2-CH_2-CH_2-OH$

27.1 70.8   69.8 25.7 25.7 68.2
$-O-CH_2-CH_2-CH_2-CH_2-O-CH_2-CH_2-CH_2-CH_2-O-C-CF_3$ (C=O)
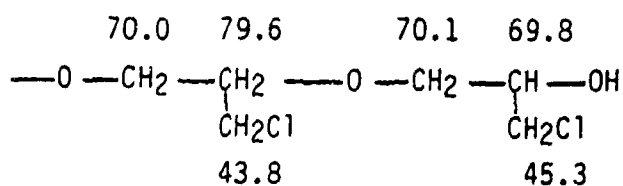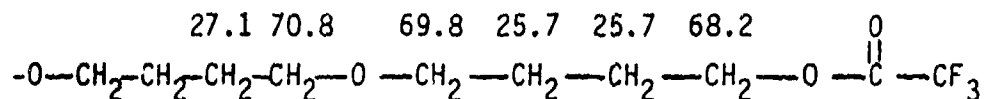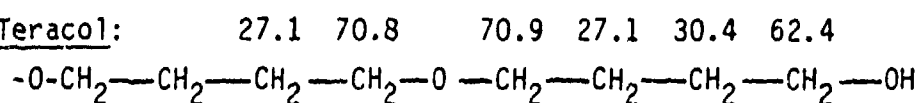
($\triangle$ ppm): α-CH$_2$ (+5.8), β-CH$_2$ (-4.7), γ-CH$_2$ (-1.4), ∂-CH$_2$ (-1.1)
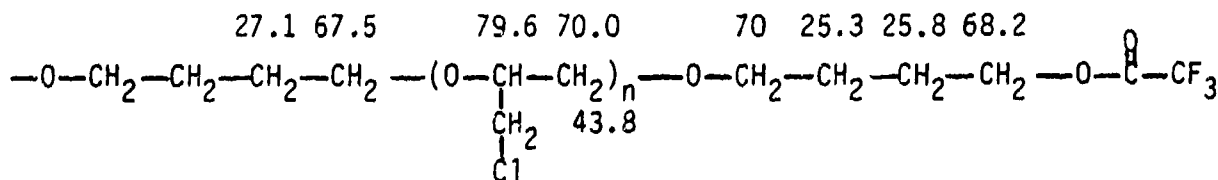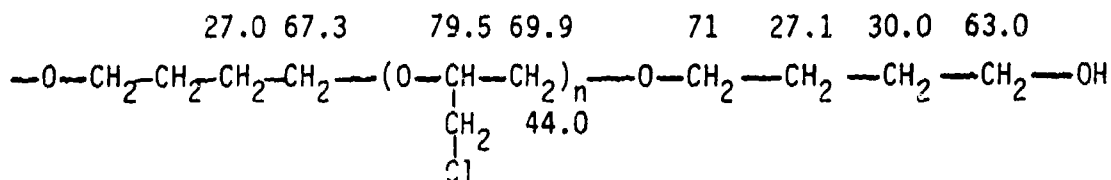
Figure 3. ^{13}C NMR (20% in C_6D_6) of Various End Groups (ppm from TMS): Change in Chemical Shifts ($\triangle$ ppm) of Neighboring Carbons When the Alcohols are Converted to the Trifluoroacetates

(a) <u>PECH-OH (I)</u>

15.8 65.8   79.5 69.9   70.9 26.9 30.3 62.6

CH_3—CH_2——$(O$—CH—$CH_2)_n$——O—CH_2—CH_2—CH_2—CH_2—OH
                     |
                   CH_2 43.7   (γ)   (β)   (α)
                   |
                   Cl

15.6   66.1   79.5 69.9   70   25.3   25.9 68.5

CH_3—CH_2—$(O$—CH—$CH_2)_n$——O—CH_2—CH_2—CH_2—CH_2—O—$\overset{O}{\overset{\|}{C}}$—$CF_3$
                 |
               CH_2 43.8
               |
               Cl

(Δppm): α-CH_2 (+5.9), β-CH_2 (-4.4), γ-CH_2 (-1.6)

(b) <u>PECH-OH (II)</u>

27.0 67.3   79.5 69.9   71   27.1   30.0 63.0

—O—CH_2—CH_2—CH_2—CH_2——$(O$—CH—$CH_2)_n$——O—CH_2—CH_2—CH_2—CH_2—OH
                             |
                          CH_2 44.0
                             |
                           Cl

27.1 67.5   79.6 70.0   70   25.3 25.8 68.2

—O—CH_2—CH_2—CH_2—CH_2—$(O$—CH—$CH_2)_n$——O—CH_2—CH_2—CH_2—CH_2—O—$\overset{O}{\overset{\|}{C}}$—$CF_3$
                          |
                       CH_2 43.8
                        |
                       Cl
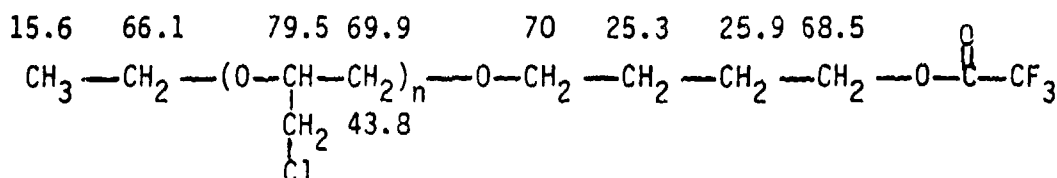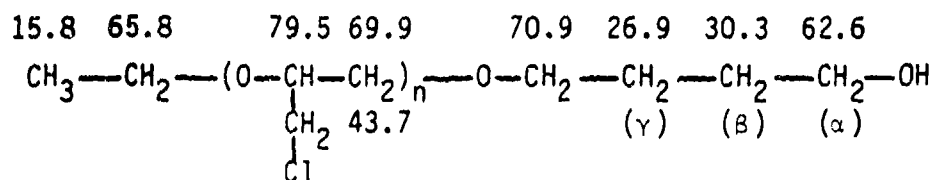
(Δppm): α-CH_2 (+5.9), β-CH_2 (-4.4), γ-CH_2 (-1.6)

Figure 4. ^{13}C NMR (20% in C_6D_6) of PECH-OH: Change in Chemical Shifts (Δppm) of Neighboring Carbons When the Alcohols are Converted to the Trifluoroacetates (20% in C_6D_6)
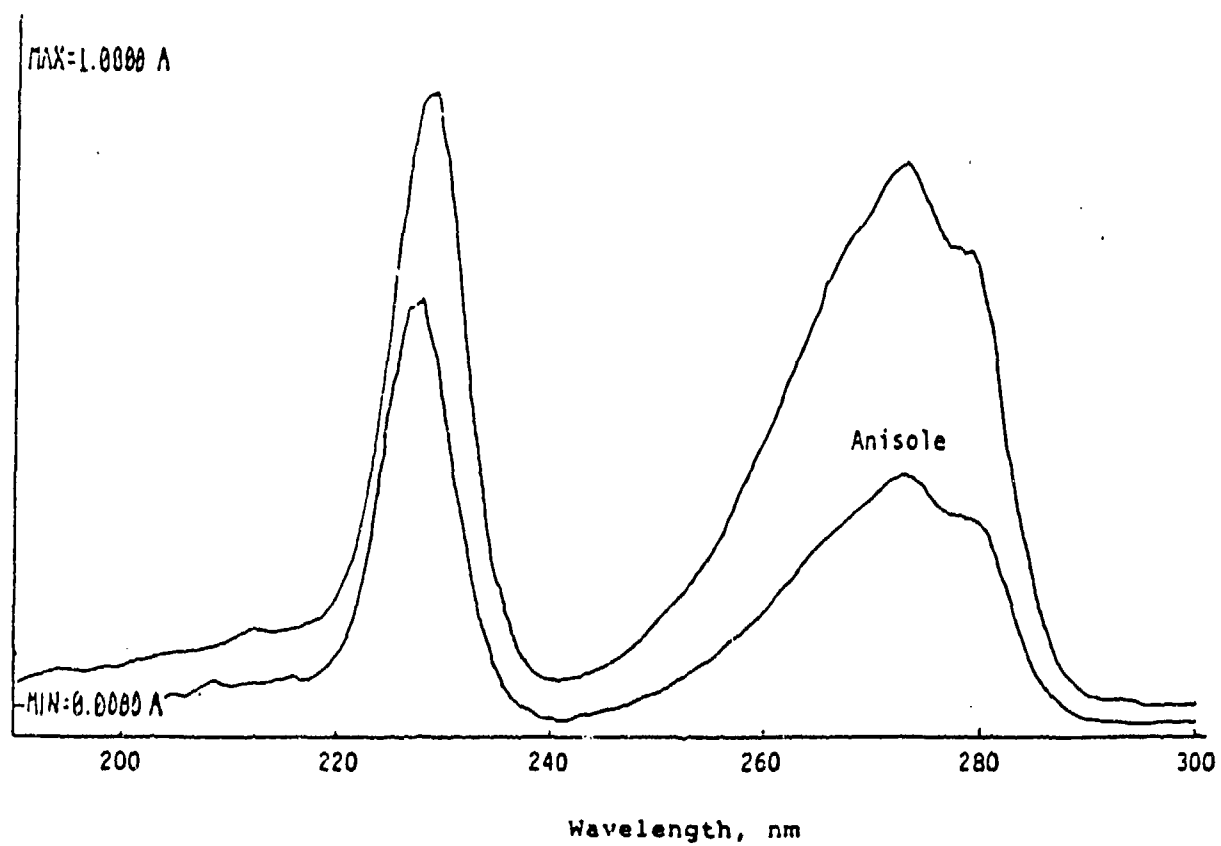
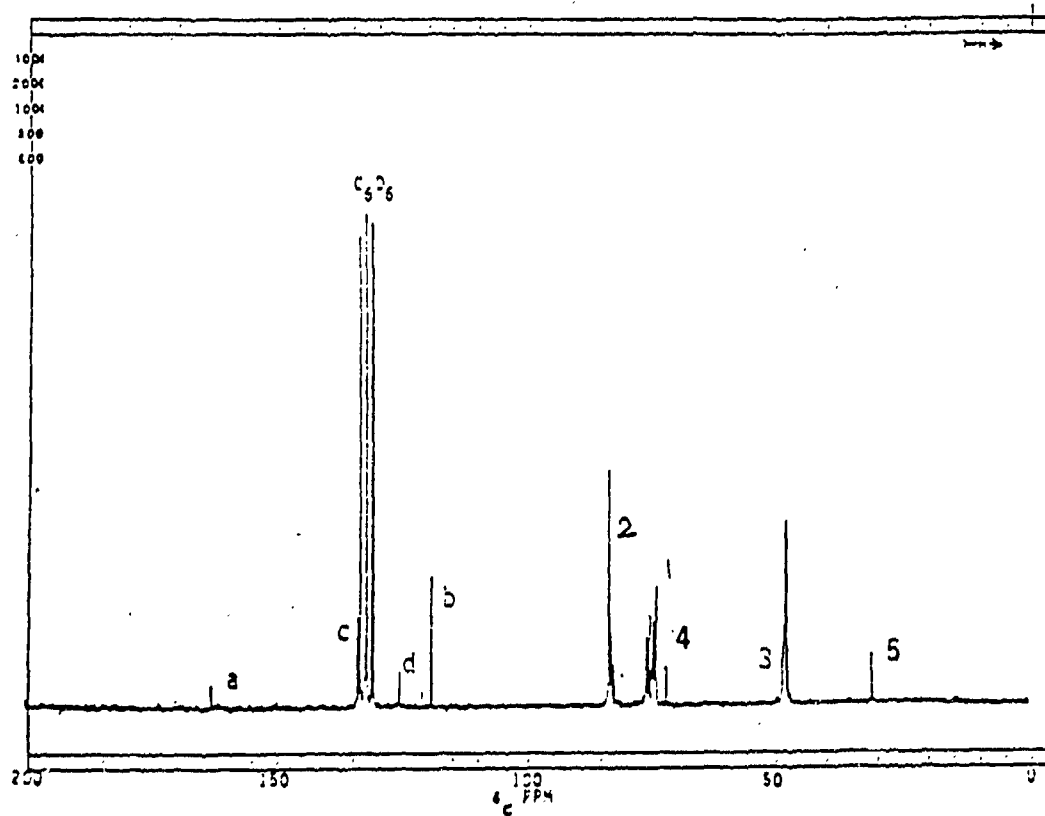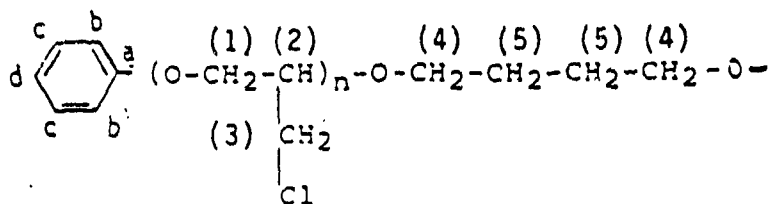Figure 5. UV Absorption Spectra of PECH-OPh and Anisole

Assignment of Peaks:

$$\text{(O-CH}_2\text{-CH})_n\text{-O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$$

with the phenyl ring labeled c, b, a, d, b', c', the side group $\overset{|}{\text{CH}_2}$ labeled (3), and Cl below; numbers (1) (2) over O-CH$_2$-CH, (4) (5) (5) (4) over the CH$_2$ groups.

Figure 6. ^{13}C NMR of PECH Terminated with Potassium phenoxide (30% w/w in C$_6$D$_6$ at 25°C).
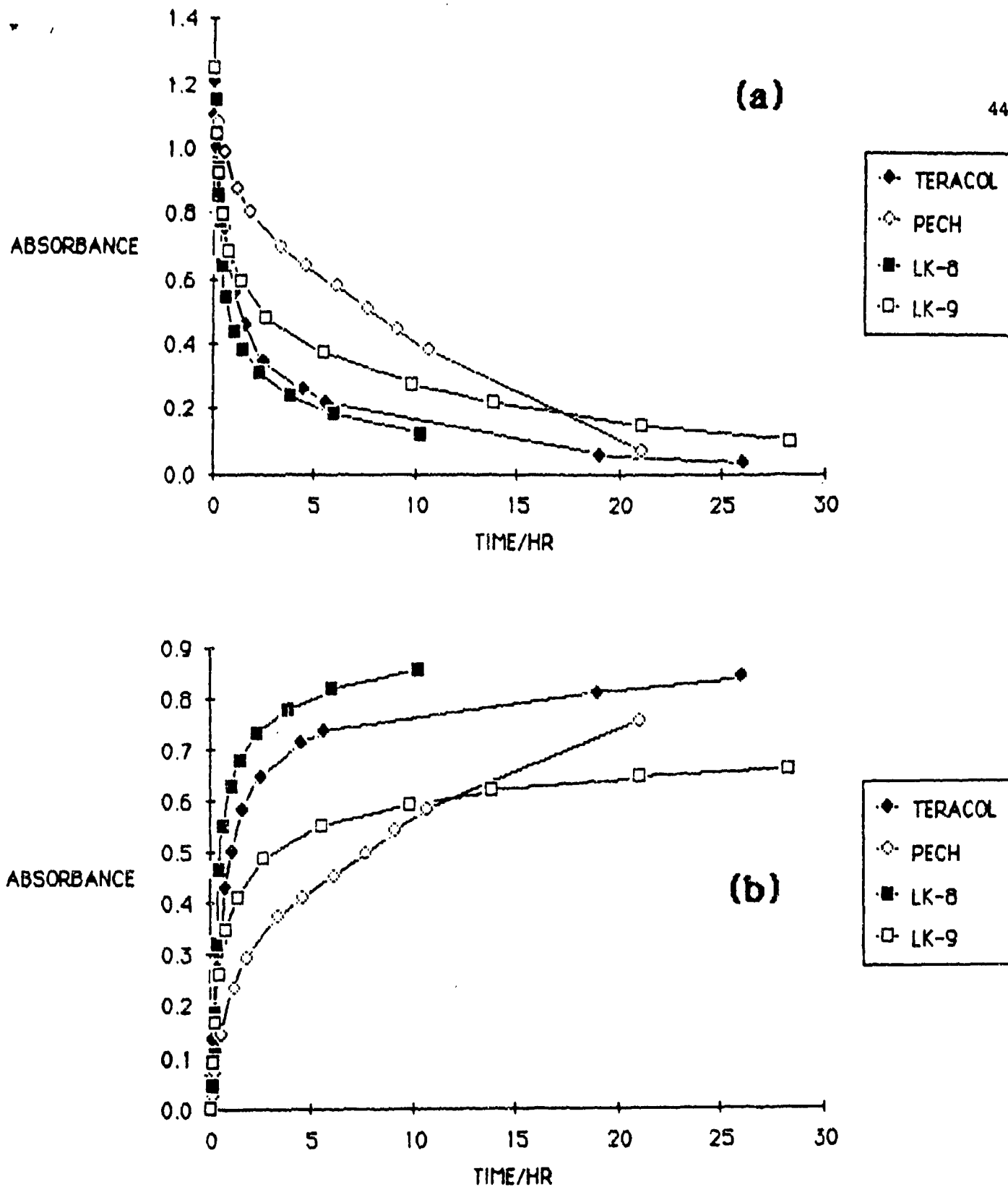
Figure 7. PECH-OH ([OH]o = 60 meq/L) + n-butyl isocyanate
([NCO]o = 70 meq/L) + FeAA3 in DCE at 41 °C;
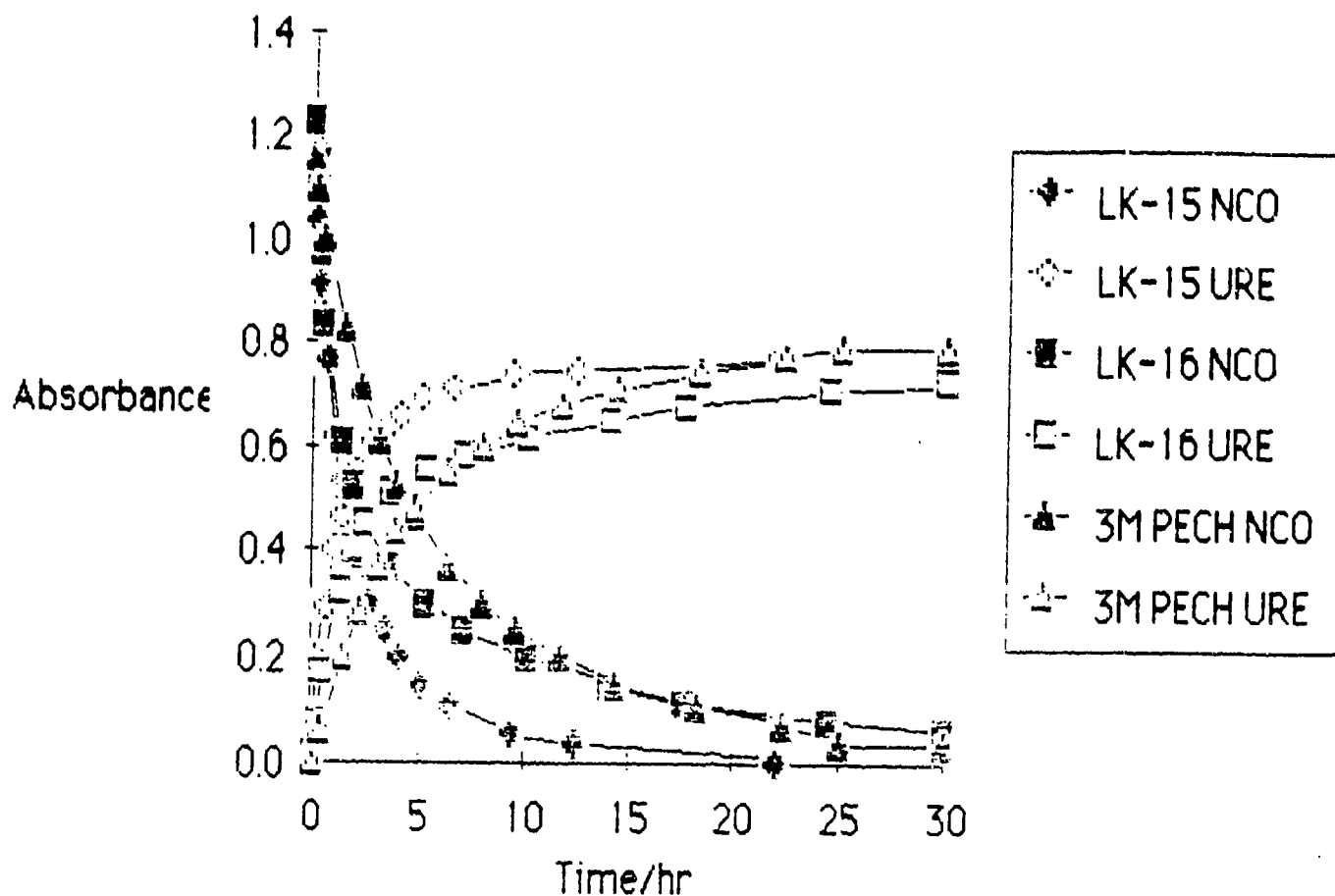(a) Isocyanate Disappearance
(b) Urethane Formation

LK-15 NCO

Figure 8.   PECH-OH ([OH]o = 60 meq/L) + n-butyl isocyanate
([NCO]o = 70 meq/L) + FeAA3 in DCE at 41 °C.